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From: carolw@alaskalife.net [mailto:carolw@alaskalife.net]
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EVALUATION OF COPPER-DISSOLVED ORGANIC MATTER BINDING IN SURFACE WATERS AT THE PROPOSED PEBBLE MINE IN ALASKA

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The Pebble Mine project is a world-class proposed copper and gold mine in southwestern Alaska that is upstream of one of the most productive salmon fisheries in the world. Understanding the bioavailability and toxicity of copper to salmonids is critical for evaluating the potential environmental effects of the development of this mine. Calcium, pH and dissolved organic matter (DOM) exert the primary controls on copper toxicity through geochemical processes related to competition for fish gill uptake sites and the formation of less toxic complexed copper species (free copper is the most toxic). The strength and abundance of DOM's metal binding sites can influence copper toxicity.

To understand and quantify copper-DOM binding in waters at the proposed Pebble Mine site, we isolated DOM from three rivers on the site – the North Fork Koktuli, Upper Talarik, and South Fork Koktuli Rivers – and measured the strength of copper binding by DOM using two methods. The three rivers had low dissolved organic carbon concentrations (2.6-4.4 mg C/L) and low alkalinity. Hydrophobic acids (humic and fulvic acids) were isolated from the three river waters for the copper binding studies, which were conducted at pH 6.0. An ion-selective electrode was used to measure free copper for copper titrations that spanned a Cu:DOM ratio of 0.003-0.3. For the copper titrations, conditional binding constants were determined for a two-ligand model using FITEQL. Similar binding constants were found for the three river waters: a log K of 6.9-7.2 and a

$\log K_2$ of 4.7-5.4. For Cu:DOM ratios closer to baseline conditions (0.0001 to 0.01), competitive ligand exchange-solid phase extraction (CLE-SPE) experiments were conducted to measure conditional binding constants. The strength of copper binding to the DOM isolates increased as the ratio of Cu:DOM decreased. The conditional binding constants were used to model copper bioavailability to resident fish populations under baseline and potential operational conditions for the proposed Pebble Mine project.

INDEPENDENT BASELINE WATER QUALITY CHARACTERIZATION OF THE PEBBLE PROJECT AREA IN SOUTHWESTERN ALASKA

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Independent investigations of the Pebble Project in southwestern Alaska have examined baseline water quality conditions in streams draining the Pebble site. The Pebble Project is one of the largest copper/gold deposits in the world and is upstream of one of the most important salmon fisheries in Alaska and globally. The baseline geochemistry sampling, which has been coordinated with baseline fisheries and aquatic invertebrate surveys, includes sampling of surface water locations during (May) and after (June) ice break-up in 2009 and after ice break-up in July 2010. The waters that flow through the Pebble region are cold, well oxygenated, and have low concentrations of dissolved solutes. Metal concentrations increased briefly during ice break-up. Most of the waters are calcium-bicarbonate dominant, but low in alkalinity and hardness. Alkalinity and pH were strongly correlated with concentrations of cations, primarily calcium, and inversely correlated with metals. Waters north of the mine lease area (Kaskanak watershed) were found to generally have higher pH and alkalinity values than the South and North Forks of the Koktuli. The water chemistry is influenced by both groundwater and surface runoff. The degree of change in concentrations of calcium and other parameters allowed us to tentatively distinguish streams that are more influenced by groundwater versus those primarily fed by surface runoff. The same methods confirmed that interbasin-transfer of water is important in the area, for example from South Fork Koktuli to an Upper Talarik tributary. The baseline water quality data indicate that waters in and around the proposed Pebble Mine site have very low concentrations of metals, even near the ore body. Waters are also low in parameters that can moderate the toxicity of metals such as alkalinity, calcium, and DOC. Future studies will assess the relationships between water chemistry and fish life stages. Particular attention will be paid to upwelling sites, which are favored by salmon and provide a conduit for transport of mine-related contaminants.

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